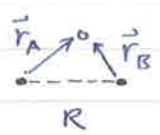


VARIABLE SEPARATION FOR H_2^+ WAVEFUNCTION

The hamiltonian for the electronic motion in H_2^+ is given by

$$\hat{H}_d = -\frac{1}{2} \nabla^2 + \frac{e^2}{R} - \frac{e^2}{|\vec{r} - \vec{R}/2|} - \frac{e^2}{|\vec{r} + \vec{R}/2|}$$

$\left. \begin{array}{l} \\ \end{array} \right\} \equiv r_A$
 $\left. \begin{array}{l} \\ \end{array} \right\} \equiv r_B$



Define two new variables

$$\xi = \frac{1}{R} (r_A + r_B) \quad \eta = \frac{1}{R} (r_A - r_B) \quad \text{and the azimuthal}$$

angle ϕ in the plane \perp to the internuclear axis (the z -axis).

The ∇^2 operator in these coordinates becomes

$$\nabla^2 = \frac{4}{R^2 (\xi^2 - \eta^2)} \left\{ \frac{\partial}{\partial \xi} \left[(\xi^2 - 1) \frac{\partial}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial}{\partial \eta} \right] + \frac{\xi^2 - \eta^2}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2}{\partial \phi^2} \right\}$$

Note, that these ^{new} variables are all dimensionless, and the spatial scale of the problem is set by the value of R . The range of the variables is $0 \leq \xi \leq \infty$, $-1 \leq \eta \leq +1$, $0 \leq \phi \leq 2\pi$, $1 \leq \xi \leq \infty$ (ξ, η, ϕ)
The variables form the confocal elliptic coordinates

Variable-separation is effected by writing the wavefunction in the form $\Phi = X(\xi) Y(\eta) Z(\phi)$ where $Z(\phi) = e^{im\phi}$ $m = 0, \pm 1, \dots$

The functions X and Y satisfy the equations

$$\frac{d}{d\xi} \left[(\xi^2 - 1) \frac{dX}{d\xi} \right] + \left[\frac{R^2}{2} \left(E - \frac{1}{R} \right) \xi^2 + 2R\xi - \frac{m^2}{\xi^2 - 1} + \mu \right] X = 0$$

$$\frac{d}{d\eta} \left[(1 - \eta^2) \frac{dY}{d\eta} \right] + \left[\frac{R^2}{2} \left(E - \frac{1}{R} \right) \eta^2 + \frac{m^2}{1 - \eta^2} + \mu \right] Y = 0$$

The Schrödinger equation is

$$\frac{\partial}{\partial \xi} \left[(\xi^2 - 1) \frac{\partial \Phi}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial \Phi}{\partial \eta} \right] + \left[\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right] \frac{\partial^2 \Phi}{\partial \phi^2} + \left[\frac{R^2}{2} \left(E - \frac{1}{R} \right) (\xi^2 - \eta^2) + 2R\xi \right] \Phi = 0$$

μ is the separation constant.

The solutions are characterised by three quantum numbers λ, n_x, n_y which are the number of zeros of the three separated functions.

A peculiarity arising out of the separation is that for a given λ , there can be two $E(R)$ curves corresponding to different pairs of (n_x and n_y) which cross each other. That is, for a given λ

$$E(R; n_x, n_y) = E(R; n'_x, n'_y) \text{ for some } R.$$

The two equations above can be solved numerically. The curve $E(R)$ can be obtained from these for both, the Φ_g and Φ_u states

The $E_u(R; 1s)$ curve from this calculation matches the curve which we obtained earlier by constructing Φ_u using LCAO

The $E_g(R; 1s)$ curve lies lower and has a minimum at a smaller value of R_0 than the curve based on constructing Φ_g using LCAO.

12 MAR 2018

WAVEFUNCTION FOR H₂

The Hamiltonian for the H₂ molecule is

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{-e^2}{|\vec{r}_1 - \vec{R}|} + \frac{-e^2}{|\vec{r}_2 - \vec{R}/2|} + \frac{-e^2}{|\vec{r}_1 + \vec{R}/2|} - \frac{e^2}{|\vec{r}_2 + \vec{R}/2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{R}$$

The Schrödinger equation with this Hamiltonian cannot be solved exactly, nor is the separation of variables possible.

We therefore use an approach similar to the one that we used for atoms to obtain the approximate wavefunction.

In atoms we constructed the many-electron wavefunction by a linear combination of single electron (atomic) wavefunctions which, ^{were} ~~in combination~~ combined with the correct spin wave functions, obeying Pauli's exclusion principle.

|| Likewise we construct the molecular wavefunctions by linear combinations of 1-electron Molecular Orbital wavefunctions, in combination with appropriate spin functions:

|| The spin wavefunction for a 2-electron system is either a singlet (S=0) or a triplet (S=1) corresponding to the functions

$$\left[\begin{array}{l} \chi_{00} = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad \underline{(S=0)} \quad m_s = \frac{1}{2} \quad -\frac{1}{2} \\ \chi_{10} = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \quad \underline{(S=1)} \quad m_s = \frac{1}{2} \quad -\frac{1}{2} \\ \chi_{11} = \alpha(1)\alpha(2) \quad \underline{(S=1)} \quad m_s = \frac{1}{2} \quad \frac{1}{2} \\ \chi_{1-1} = \beta(1)\beta(2) \quad \underline{(S=1)} \quad m_s = -\frac{1}{2} \quad -\frac{1}{2} \end{array} \right.$$

1-electron

Recall that the (spatial) molecular orbital wavefunctions are

$$\Phi_g(R, r) = \frac{1}{\sqrt{2}} (\psi(r_A) + \psi(r_B))$$

$$\Phi_u(R, r) = \frac{1}{\sqrt{2}} (\psi(r_A) - \psi(r_B))$$

and Φ_g corresponds to the lowest energy when $\psi(r_A, B) \equiv \psi_{1s}(r_A, B)$

MOLECULAR ORBITAL METHOD

In accordance with the exclusion principle, states corresponding to χ_{00} must have an antisymmetric spatial part, and there are three ~~such~~ possible linear combinations of molecular orbitals. for the singlet state

$$\begin{aligned}\Psi_A(1,2) &= \Phi_g(1) \Phi_g(2) \chi_{00}(1,2) && {}^1\Sigma_g^+ \text{ state of } H_2 \\ \Psi_B &= \Phi_u(1) \Phi_u(2) \chi_{00}(1,2) && {}^1\Sigma_g^+ \text{ state of } H_2 \\ \Psi_C &= \frac{1}{\sqrt{2}} [\Phi_g(1) \Phi_u(2) + \Phi_u(1) \Phi_g(2)] \chi_{00}(1,2) && {}^1\Sigma_u^+ \text{ state of } H_2\end{aligned}$$

and only one possibility for the triplet state with anti-symmetric spatial part:

$$\Psi_D(1,2) = \left. \begin{aligned} &\frac{1}{\sqrt{2}} [\Phi_g(1) \Phi_u(2) - \Phi_g(2) \Phi_u(1)] \chi_{11}(1,2) \\ &\frac{1}{\sqrt{2}} [\chi_{1-1}(1,2) \\ &\frac{1}{\sqrt{2}} [\chi_{10}(1,2) \end{aligned} \right\} {}^3\Sigma_u^+ \text{ stat of } H_2$$

The first case^(A) corresponds to the lowest energy.

To obtain the energies corresponding to these states we re-write the Hamiltonian in the form

$$\hat{H}_0 = H_0(1) + H_0(2) + \frac{1}{r_{12}} + \frac{1}{R}$$

$$\text{where } H_0(i) = -\frac{1}{2} \nabla_i^2 - \frac{1}{|\vec{r}_i - \vec{R}/2|} - \frac{1}{|\vec{r}_i + \vec{R}/2|} \quad (i=1,2)$$

($\equiv r_{iA}$) ($\equiv r_{iB}$)

This ensures that the 1-electron molecular orbital wavefunctions are exact solutions to

$$\hat{H}_{0i} \Phi_{g,u} = \left[E_{g,u} - \frac{1}{R} \right] \Phi_{g,u}$$

The $\Phi_{g,u}$ are assumed normalised to 1, so that

$$\begin{aligned} E &= \int \Psi_A^* \hat{H} \Psi_A d\tau_1 d\tau_2 \\ &= 2E_g(R) - \frac{1}{R} + \int \frac{|\Phi_g(1) \Phi_g(2)|^2}{r_{12}} d\tau_1 d\tau_2 \end{aligned}$$

↑
numerical integration

recalling that $\Phi_g = [\psi_{1s}(r_A) + \psi_{1s}(r_B)] / \sqrt{2}$, so that

$$\Phi_g(1) = \frac{\psi_{1s}(r_{A1}) + \psi_{1s}(r_{B1})}{\sqrt{2}} ; \quad \Phi_g(2) = \frac{\psi_{1s}(r_{A2}) + \psi_{1s}(r_{B2})}{\sqrt{2}}$$

we have

$$\Psi_A = \frac{1}{2} \left[\psi_{1s}(r_{A1}) \psi_{1s}(r_{B2}) + \psi_{1s}(r_{A2}) \psi_{1s}(r_{B1}) + \psi_{1s}(r_{A1}) \psi_{1s}(r_{A2}) + \psi_{1s}(r_{B1}) \psi_{1s}(r_{B2}) \right] \chi_{00}(1,2)$$

The first two terms correspond to the case when the two electrons are equally shared (associated with) between the nuclei

The second two terms correspond to the case when the two electrons are more likely associated with one nucleus than being shared.

The first two terms therefore represent "covalent bonding"

$$\Psi_A^{\text{covalent}} \equiv \frac{1}{2} \left[\psi_{1s}(r_{A1}) \psi_{1s}(r_{B2}) + \psi_{1s}(r_{A2}) \psi_{1s}(r_{B1}) \right] \chi_{00}(1,2)$$

while the other two represent ionic bonding

$$\Psi_A^{\text{ionic}} = \frac{1}{\sqrt{2}} \left[\psi_{1s}(r_{A1}) \psi_{1s}(r_{A2}) + \psi_{1s}(r_{B1}) \psi_{1s}(r_{B2}) \right] \chi_{00}(1,2)$$

The probability corresponding to Ψ^{ionic} is smaller than that for Ψ^{covalent} . The ionic part represent the case of $H^+ : H^-$ separated atoms limit, while the covalent part represents the $H:H$ separation limit.

The Ψ_A^{covalent} wavefunction by itself is an LCAO of two atomic hydrogen wavefunctions with exchange, corresponding to the singlet state $^1\Sigma_g^+$. Similarly, (if we expand out the Ψ_D^B written earlier for the $^3\Sigma_u^+$ state), we find that there is a similar "covalent" part

$$\Psi_D^{\text{cov.}} = \frac{1}{2} \left[\psi_{1s}(r_{A1}) \psi_{1s}(r_{B2}) - \psi_{1s}(r_{A2}) \psi_{1s}(r_{B1}) \right] \chi_{11} \quad \left(\begin{array}{l} \text{three} \\ \text{spin} \\ \text{states} \end{array} \right)$$

In both the above wavefunctions, $\Psi_A^{\text{cov.}}(^1\Sigma_g^+)$ and $\Psi_D^{\text{cov.}}(^3\Sigma_u^+)$ there is a direct linear combination of atomic hydrogen 1s states

(both atoms are separately 1s). These resultant molecular orbitals are called Valence-Bond or Heitler-London orbitals.

The corresponding energies of the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ states are given by

$$E_{g,u} = 2E_{1s} \pm \frac{J}{1 \pm I^2} \pm \frac{K}{1 \pm I^2} + \frac{1}{R}$$

where

$$I = \int \psi_{1s}(r_{A1}) \psi_{1s}(r_{B1}) d\tau_1 = \int \psi_{1s}(r_{A2}) \psi_{1s}(r_{B2}) d\tau_2$$

$$J = \int |\psi_{1s}(r_{A1})|^2 |\psi_{1s}(r_{B2})|^2 d\tau_1 d\tau_2 \left(\frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} \right)$$

$$K = \int \psi_{1s}(r_{A1}) \psi_{1s}(r_{B2}) \left(\frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} \right) \psi_{1s}(r_{A2}) \psi_{1s}(r_{B1}) d\tau_1 d\tau_2$$